

# FORMATION OF AROMATIC HYDROCARBONS DUE TO PARTIAL OXIDATION REACTIONS IN BIOMASS GASIFICATION

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## ABSTRACT

Biomass gasification is primarily a gas phase process due to its high reactivity, with 90% direct (primary) conversion to volatile material under high heat transfer conditions. Subsequent, vapor-phase (secondary) pyrolysis and oxidation reactions lead to the formation of gaseous products, such as hydrogen and carbon monoxide, and condensable materials, such as polynuclear aromatic hydrocarbons. This paper reports the results of studies of vapor-phase thermal and oxidative pathways for major biomass constituents under typical gasification conditions. Carbohydrate-derived primary products, including anhydrosugars, low-molecular-weight aldehydes and furan and pyran derivatives are converted into a different distribution of products in the presence of low levels of oxygen. Enhanced conversions of alcohols to aldehydes are observed. Major oxidation products include formaldehyde, ketene, acrolein and furan. Lignin-derived volatiles are methoxyphenols, which undergo a greater cracking rate to aromatics and phenolics in the presence of oxygen.

## INTRODUCTION

Biomass gasification is a complex combination of pyrolysis and oxidation reactions in the condensed and vapor phases. Evans and Milne [1,2] identified reaction regimes and characterized the gaseous constituents present and the nature of the major solid- and vapor-phase reactions. The product distribution in each regime is a function of process variables, such as oxygen level, steam-to-biomass ratio, pressure, and the time and temperature history of the solid and gaseous materials. Under typical gasification conditions, oxygen levels are restricted to less than 30% of that required for complete combustion (including the oxygen in the wood), and CO and H<sub>2</sub> are the major products. This paper describes the organic products that typically are formed and presents the changes in product composition as a function of reaction severity. The goal of this work is to develop an understanding of the chemical and physical processes of biopolymer pyrolysis and oxidation leading to aromatic hydrocarbon formation.

Evans and Milne [1-3] used molecular beam mass spectrometry (MBMS) to suggest that a systematic approach to classifying pyrolysis products as primary, secondary, and tertiary products can be used to compare products from the various reactors that are used for pyrolysis and gasification. Four major product classes were identified as a result of gas-phase thermal cracking reactions:

1. Primary products characterized by cellulose-derived products, such as levoglucosan, hydroxyacetaldehyde, and furfurals; analogous hemicellulose-derived products, and lignin-derived methoxyphenols;
2. Secondary products characterized by phenolics and olefins;
3. Alkyl tertiary products that include methyl derivatives of aromatics, such as methyl acenaphthylene, methyl naphthalene, toluene, and indene;
4. Condensed tertiary products that show the polynuclear series without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, and pyrene.

In this paper we report the study of carbohydrates and lignin studied at three temperatures under pyrolysis and partial oxidation conditions. The three temperatures and gas phase residence times were selected to correspond to primary, secondary and tertiary regimes.

## EXPERIMENTAL

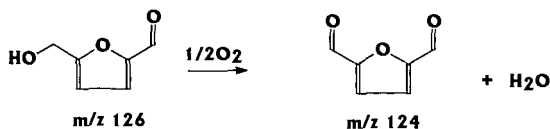
Small scale, batch pyrolysis experiments are conducted in tubular reactors by introducing a sample of biomaterial into flowing gas that is preheated to the temperature of interest. The composition of the flowing gas is typically helium for pyrolysis and He/oxygen mixtures for oxidative studies. Oxygen can be introduced after the sample to focus on gas-phase oxidation. For primary pyrolysis, the products of the initial pyrolysis step are sampled as rapidly as possible with a residence time of less than 50 ms. In the work reported here, primary conditions are at a temperature of 500 °C and a residence time of 50 ms. Gas-phase reaction time is added to achieve secondary and tertiary conditions. To enhance mixing and to achieve isothermal conditions, a tubular reactor packed with quartz chips was used to give a residence time of 250 ms. Secondary and tertiary reactions were performed at 650 °C and 750 °C, respectively. For oxidation studies, the oxygen was included in the gas before preheating for primary conditions,

but was added after the sample for secondary and tertiary studies. A level of 5% by volume was used for partial oxidation.

The analysis of the products was performed in real time with the NREL molecular beam mass spectrometry technique (MBMS) [1-3]. Illustrative data are shown in Figs. 1-2. These data are processed by averaging the spectra that are acquired over the pulse from the batch experiments. Collision induced dissociation (CID) experiments were conducted in the same way and the first quadrupole mass filter of the MBMS was tuned to only pass the ion of interest. A second quadrupole is used as a collision cell by introducing argon gas. Collisions between the energetic ions and the argon result in fragments that are introduced into a third quadrupole mass filter for analysis of the dissociation products.

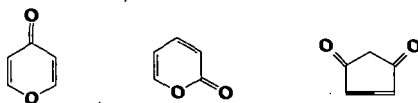
## RESULTS AND DISCUSSION

All materials were screened at three temperatures for both pyrolysis and oxidation. The carbohydrates studied were cellulose, glucose, sucrose, levoglucosan and pectin. The results for sucrose are shown in fig. 1. Pyrolysis causes the cracking to low molecular weight products. The oxidation results show the formation of ions at  $m/z$  124, 96, 68, 56, 42 and 30. This series is common to all the carbohydrates studied under these conditions. The  $m/z$  124 is derived from  $m/z$  126 and is probably formed by the oxidation (dehydrogenation) of the alcohol function of 5-hydroxymethyl furfural to form a di-aldehyde.



Analysis of  $m/z$  124 by CID shows major peaks at  $m/z$  39, indicating retention of the furan ring, and  $m/z$  123, showing loss of one hydrogen, which is characteristic of aldehydes. This same reaction occurs to a lesser extent in pyrolysis reactions. An interesting question is the extent that the reaction under pyrolysis conditions is the result of hydrogen abstraction from other pyrolysis products.

The predominance of  $m/z$  96 at 650 °C and 5%  $\text{O}_2$  is significant since CID analysis shows that this is not due entirely to furfural. In addition to  $m/z$  95 and 39, which are the main daughters from furfural, the carbohydrates under these conditions show additional peaks at  $m/z$  97, 41 and 69. The  $m/z$  97 is an  $M+1$  peak, which shows that ion-molecule reactions must be occurring in the collision cell, possibly between the aldehyde hydrogen in furfural and the other compounds at  $m/z$  96. Three additional possibilities are shown below with the same empirical formula,  $\text{C}_5\text{H}_4\text{O}_2$ , as furfural. There are probably multiple sources of the  $m/z$  96 products under these conditions, since a variety of starting materials give rise to a strong  $m/z$  96 signal. This includes levoglucosan and Avicel (which pyrolyzes to give high yields of levoglucosan) and the simple sugars and 5-HMF.



**4H-Pyran-4-one    2H-Pyran-2-one    4-Cyclopentene-1,2-dione**

An analogous dehydrogenation reaction as described above for 5-HMF occurs with hydroxyacetaldehyde (HAA) with conversion to glyoxal. Hence, the  $m/z$  60 intensity is reduced in the oxidation product slate at 650 °C and  $m/z$  58 is enhanced. Other products of interest under the oxidation regime are furan ( $m/z$  68), acrolein ( $m/z$  56), ketene ( $m/z$  42), and formaldehyde ( $m/z$  30).  $m/z$  56 is most likely to be acrolein and the CID results are supportive of this showing the loss of hydrogen in the daughter ion spectrum. The formation of butenes contributing to the signal at  $m/z$  56 is not significant, since no hydrocarbon fragments were present in the  $m/z$  40-44 range as would be expected for butenes. The formation of acrolein, ketene and formaldehyde are important observations since these species will be highly reactive and may lead to aromatics. Their formation may be difficult to follow by other analysis techniques since they may react during sample collection and handling.

The peaks at  $m/z$  18, 28, and 44 are due to water, CO, and  $\text{CO}_2$  with some possible contribution at  $m/z$  28 and 44 from other products. The CID intensities for major daughter ions of  $m/z$  44 for carbohydrates and model compounds are shown in Table 1. Under pyrolysis conditions, the daughter ions at  $m/z$  15, 43 and 45 are evidence for acetaldehyde. Under oxidation conditions however, the CID evidence is that all of  $m/z$  44 is due to  $\text{CO}_2$ .

CID of  $m/z$  126 for the carbohydrates and model compounds studies is shown with intensities for major peaks in table 2. The base peak for pectin, sucrose and glucose is  $m/z$  41 which is the same as for 5-HMF indicating that this is the major product at  $m/z$  126. All three have higher intensities at  $m/z$  126 than 5-HMF, which indicate that there is a contribution from other compounds. Trihydroxybenzenes (THB) have been identified as pyrolysis products of carbohydrates. The three isomers of THB all show base peaks at  $m/z$  126 in their CID spectra. They also show significant intensities at  $m/z$  43 as does the 1,3,5-THB isomer. The pectin CID is different than glucose and sucrose with intensities at  $m/z$ , 52 and 80 which corresponds to peaks for the 1,2,3- and 1,2,4- isomers of THB. The lack of  $m/z$  108 in the pectin spectrum indicates that the 1,2,4- isomer is the predominant of the two for pectin

Phenolic compounds were studied, including lignin, coniferyl alcohol, vanillin, catechol, phenol and guaiacol. The results for lignin are shown in fig. 2. Oxidation accelerates the cracking of the phenolics compared to pyrolysis, with much higher amounts of benzene, toluene and xylene under oxidative tertiary conditions.

## CONCLUSIONS

Paths to aromatic hydrocarbons have been shown for the major compound types studied with varying influences of temperature and the effect of oxygen. For carbohydrates, the effect of oxygen increases the rate of secondary cracking and primary pyrolysis products undergo highly specific oxidation reactions including 5-HMF to the di-aldehyde, HAA to glyoxal and a predominance of acrolein, formaldehyde, and furan. Within the kinetic regime studied, lignin and related phenolic model compounds had the highest rate of aromatic hydrocarbon formation and oxygen accelerated the rate of formation.

## REFERENCES

1. Evans, R. J. and T. A. Milne (1987) *Energy and Fuels*, 1, p. 123-137.
2. Evans, R. J. and T. A. Milne (1987) *Energy and Fuels*, 1, p. 311-.
3. Evans, R. J. and T. A. Milne (1997) in *Developments in Thermochemical Biomass Conversion* (eds. A.V. Bridgwater and D.G. B. Boocock) Blackie A&P, London, pp. 803-816.

Table 1. CID daughter Ion Intensities for M/Z 44 for pyrolysis and oxidation at 650 C.

M/Z	Levog.		HAA		Avicel		pectin		sucrose		Glucose		CO2		HAc	
	Py	Ox	Py	Ox	Py	Ox	Py	Ox	Py	Ox	Py	Ox	Py	Ox	Py	Ox
15	7	1	8	0	8	1	3	1	12	1	9	1	0	0		18
27	5	0	0	0	5	0	1	0	3	0	3	0	0	0		0
28	3	4	4	4	3	4	3	4	3	3	3	5	7	2		5
29	4	0	1	0	4	0	1	1	3	1	3	0	0	0		1
42	5	1	4	1	5	1	2	1	7	1	5	1	1	1		8
43	45	10	47	8	46	9	23	10	66	13	56	11	9	5		100
44	100	100	100	100	100	100	100	100	100	100	100	100	100	100		69
45	15	2	6	1	17	1	6	2	13	2	14	1	2	2		80

Table 2. CID daughter Ion Intensities for M/Z 126 for pyrolysis at 650 C.

	Pectin	sucrose	glucose	135-THB	123-THB	124-HB	5-HMF
39	21	13	13	3	0	2	29
41	100	100	100	6	1	3	100
43	31	38	37	29	0	3	1
52	20	7	7	15	77	84	1
69	55	67	65	23	0	3	63
80	13	4	2	7	41	37	0
85	0	0	1	28	0	0	0
97	54	72	67	2	1	5	66
108	1	1	0	0	15	3	0
125	14	13	13	4	5	8	10
126	83	68	74	100	100	100	44
127	9	8	14	7	9	9	7

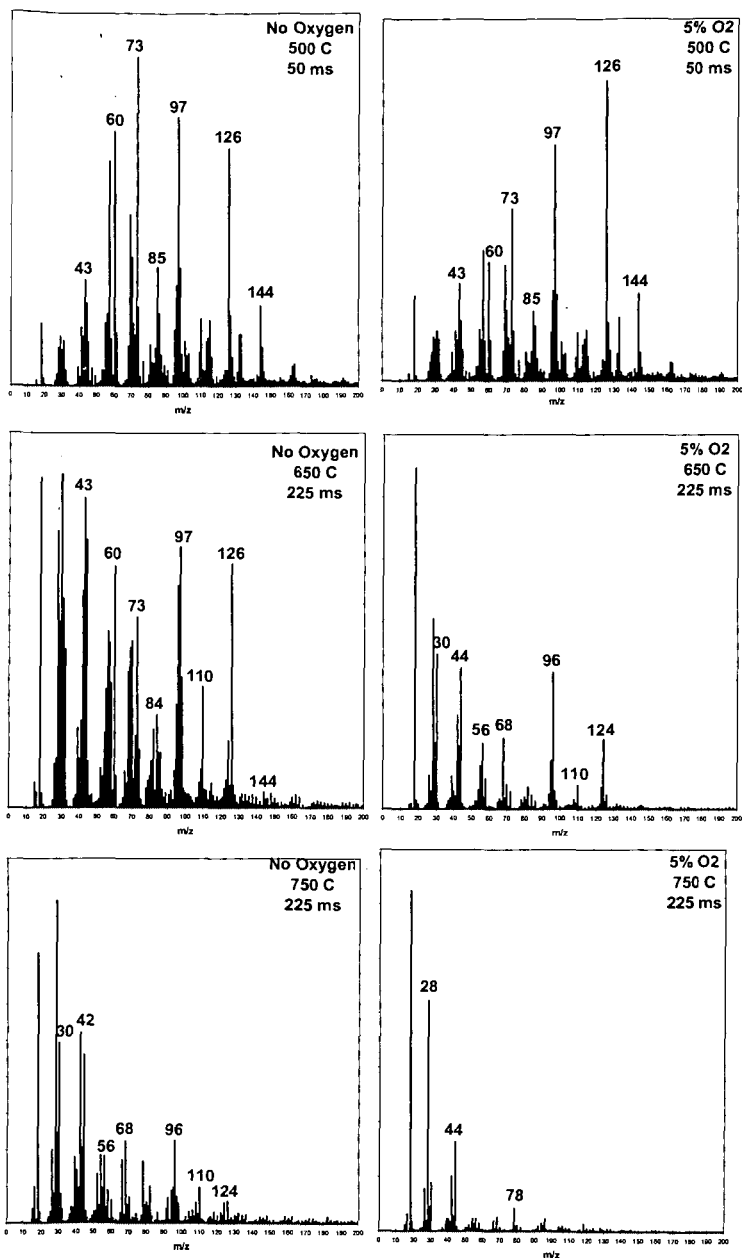


Fig. 1. Mass Spectra of Products for the pyrolysis (left) and oxidation (right) of sucrose at 550 °C (top), 650 °C (middle) and 750 °C (bottom). The 550 °C spectra are with a residence time of 50 ms. The 650 °C and 750 °C are for 225 ms residence time. The oxidation experiments were performed by injecting oxygen after the sample holder. The Oxygen level was 5% by volume.

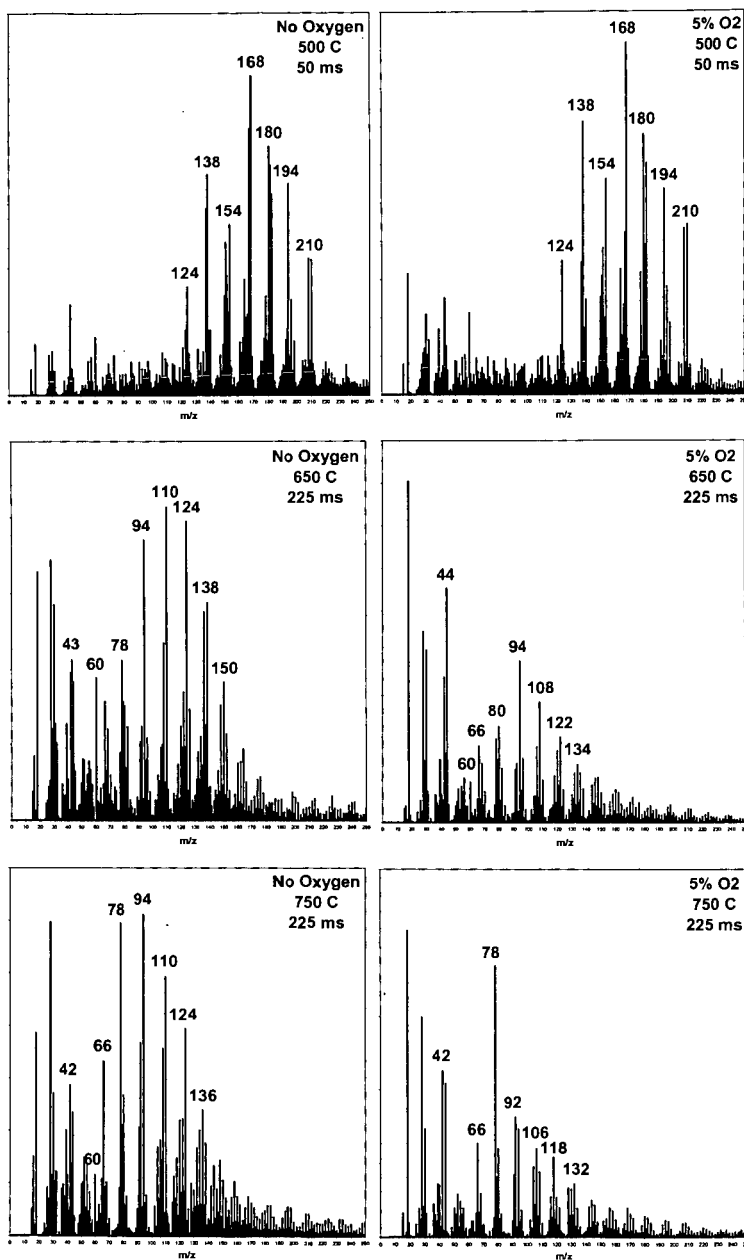


Fig. 2. Mass Spectra of Products for the pyrolysis (left) and oxidation (right) of ball milled lignin at 550 °C (top), 650 °C (middle) and 750 °C (bottom). Same conditions as Figure 1.